

Table 21.2 U.S. Uranium Energy Available
Exceeds Other Known Sources

Resource	Available Energy, EJ (10^{18} J)
Uranium	137,500
Coal and lignite	12,700
Oil shale	6,120
Petroleum and natural gas liquids	1,160
Natural gas	1,090

SOURCE: U.S. Department of Energy.

NUCLEAR FUELS

SOURCES AND RESERVES. In the early years of the nuclear industry, South African ores of various types and Canadian pitchblende were the major sources. In later years, larger supplies of uranium ore came from domestic sources as shown in Table 21.3.

Uranium is more abundant in the earth's crust than mercury and is present in about the same amount as tin and molybdenum. It is widely distributed.

Thorium, while less widely used than uranium, is a suitable nuclear fuel. A commercial thorium-fueled reactor operates at St. Vrain, Colo. and an experimental light water-moderated thorium-fueled breeder reactor is at Shippingport, Penn.

Thorium exists with only one natural isotope, ^{232}Th , and is not very rare. Most of it is obtained as a by-product of the processing of monazite, a complex phosphate, for the extraction of rare earths. Major deposits are found in India, Brazil, Union of South Africa, Australia, Malaysia, and the United States. Reserves are substantial and hardly utilized yet.

MINING AND MILLING ORE.⁷ Figure 21.3 shows the main steps from ore to usable nuclear materials. The purification utilizes an organic solvent extraction, a difficult isotope separation process, and finally a unique process—the synthesis of an element, plutonium.

The steps are:

1. Mining of the ore. Mined U.S. ores carry only a low concentration (around 0.2% U_3O_8) of uranium.

⁷Merritt, *The Extractive Metallurgy of Uranium*, Colorado School of Mines, Golden, Colo., 1971.

Table 21.3 U.S. Uranium Statistics: 1970 to 1980
(in thousands of metric tons of U_3O_8)

	1970	1975	1978	1979	1980
Recoverable U_3O_8	11.6	10.9	17.1	14.3	18.2
Production, concentrate	11.7	10.5	16.8	17.0	19.9
Imports, concentrate*	—	0.6	2.4	1.5	1.6
Free world production	22.0	22.5	40.1	44.9	51.5

*Mainly for enrichment prior to 1977.

SOURCE: U.S. Department of Energy, *Statistical Data of the Uranium Industry*, 1981 and 1980, annual report to Congress, vol. 11.

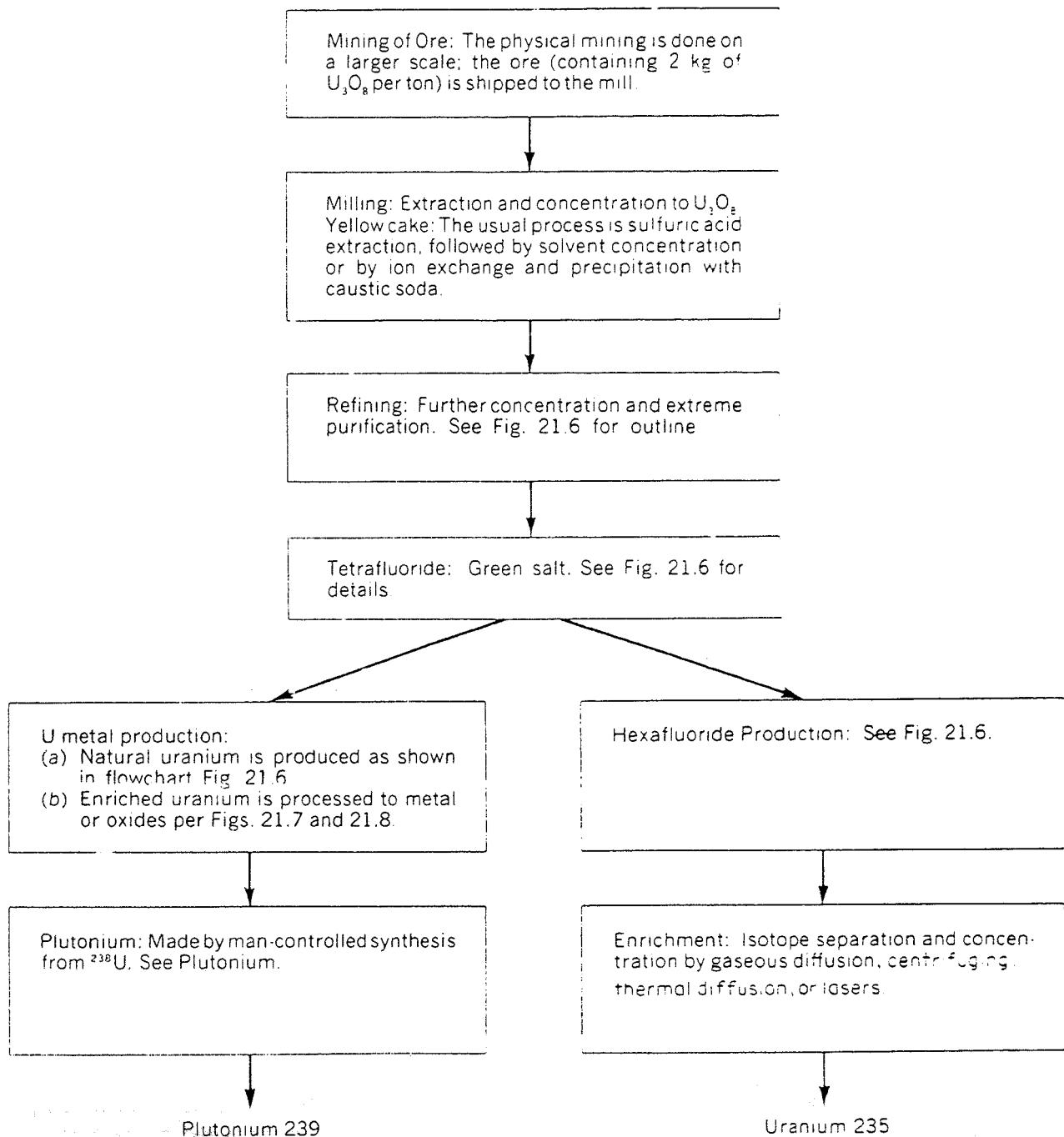


Fig. 21.3. General outline of chemical flowchart from ore to usable nuclear material

2. Milling and extraction to produce impure U₃O₈ or yellow cake. Ores are usually leached with sulfuric acid, then the weak leach solutions are concentrated by ion-exchange or solvent extraction, and finally yellow cake is precipitated with caustic soda. The tailings contain a small amount of radioactive material.
3. Refining and purification to produce extremely pure uranium by procedures outlined in Fig. 21.4. UO₂(NO₃)₂·6H₂O, UO₂, UO₃, UF₄, and UF₆ (and sometimes metallic U) are all involved.
4. Isotope enrichment in ²³⁵U, usually by separating ²³⁵UF₆ from mixed isomers of UF₆ using gas diffusion.
5. Conversion of UF₆ to UO₂ or U.
6. Nuclear fuel fabrication, generally as UO₂, UC, or U.

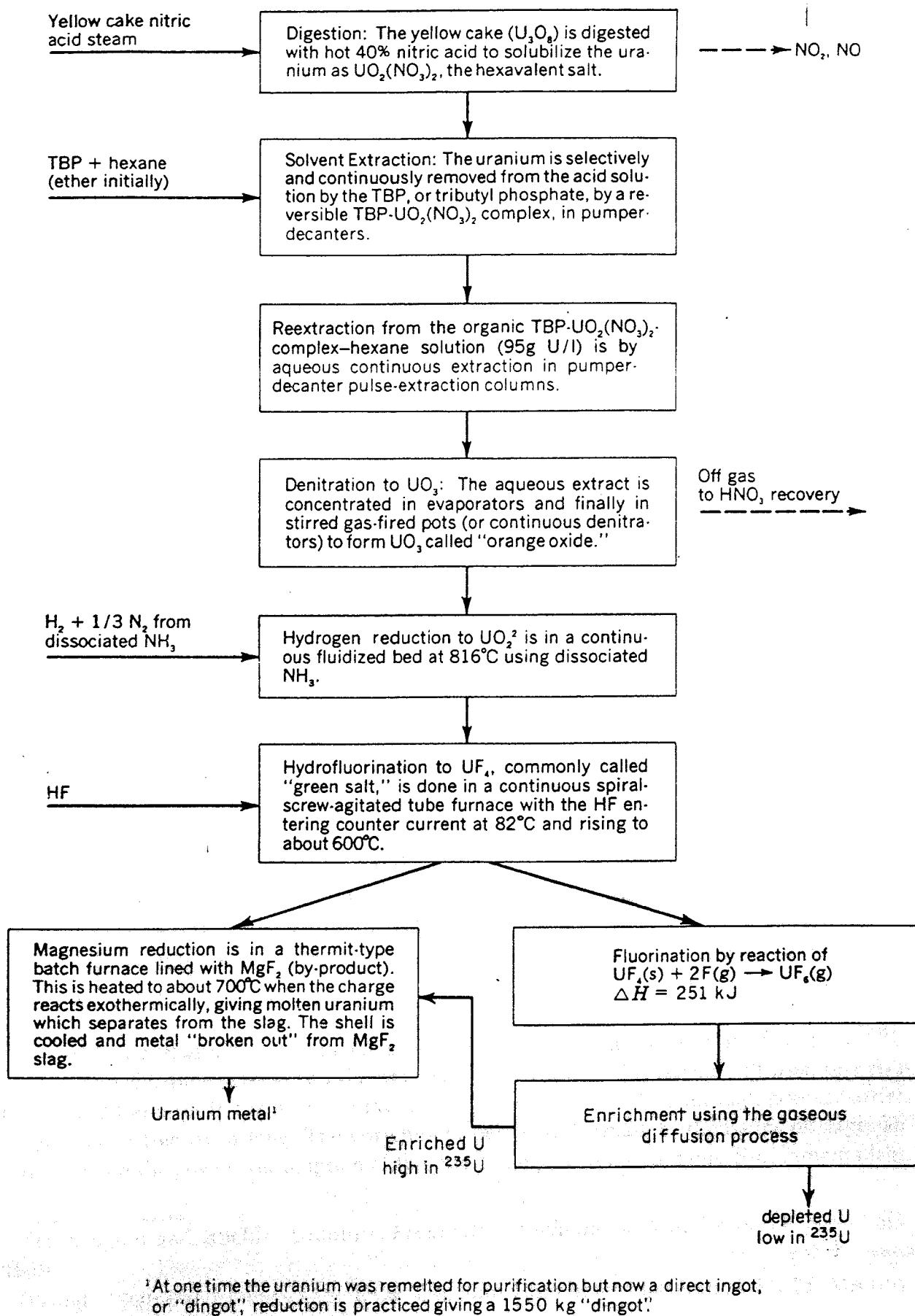


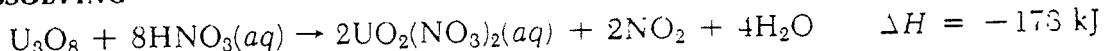
Fig. 21.4. Refining of uranium: feed-material-plant flowchart.

7. Mechanical forming, involving pressing, sintering, and grinding to precise size.
8. Element fabrication. Cladding, sealing, pressuring, and assembling into units.
9. Reaction in a nuclear reactor to produce power and/or plutonium.

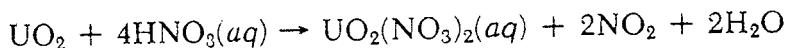
REFINING AND PURIFICATION.⁸ Conversion of crude yellow cake or uranium metal to material pure enough for reactor use, i.e., free of other elements, particularly neutron absorbers, is required. Boron and cadmium are particularly troublesome and must be below 1 ppm. The process for accomplishing this was a closely guarded secret until the end of World War II. Figure 21.4 shows the essential steps of the process as operated at Savannah River, S.C. or Hanford, Wash. Uranyl nitrate hexahydrate is quite soluble in ethyl ether, tributyl phosphate-kerosene, or TBP-hexane solutions. Contaminants show virtually no solubility. These extractions make a very clean separation of uranium from other inorganics possible, yielding high purities with few steps. This organic extraction procedure is also useful in treating irradiated fuel elements from reactors to separate uranium and plutonium.

The reactions involved are as follows.

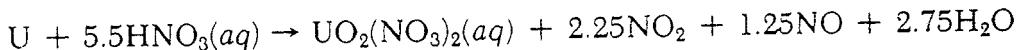
DISSOLVING



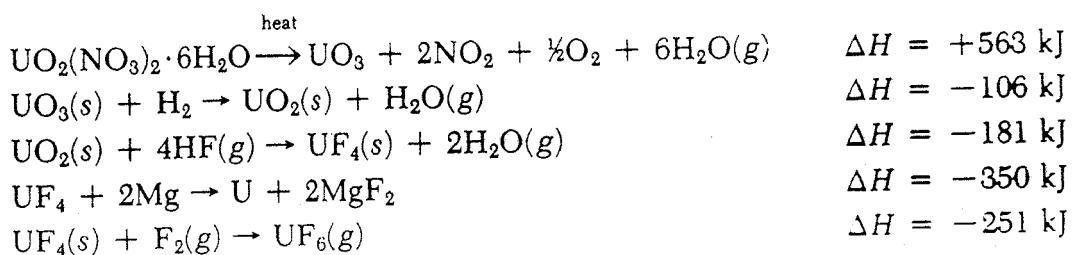
or



or



Solvent extraction then yields very pure uranium nitrate hexahydrate, which is converted to volatile UF_6 by the following reactions:



ISOTOPE ENRICHMENT.⁹ Two major processes are used today to separate ^{235}U from ^{238}U : The gaseous diffusion process and the gas centrifuge process. The gaseous diffusion process is based on differences in the diffusion rate between $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ through porous barriers several mean free paths long. The enrichment per stage is small, so thousands of stages are required and the power consumption of the interstage pumps is enormous. Enrichment plants

⁸Harrington and Ruehle, *Uranium Production Technology*, Van Nostrand, New York, 1959.

⁹Voigt, "Status and Plans of the DOE Uranium Enrichment Program," AIChE Meeting, March 1982.

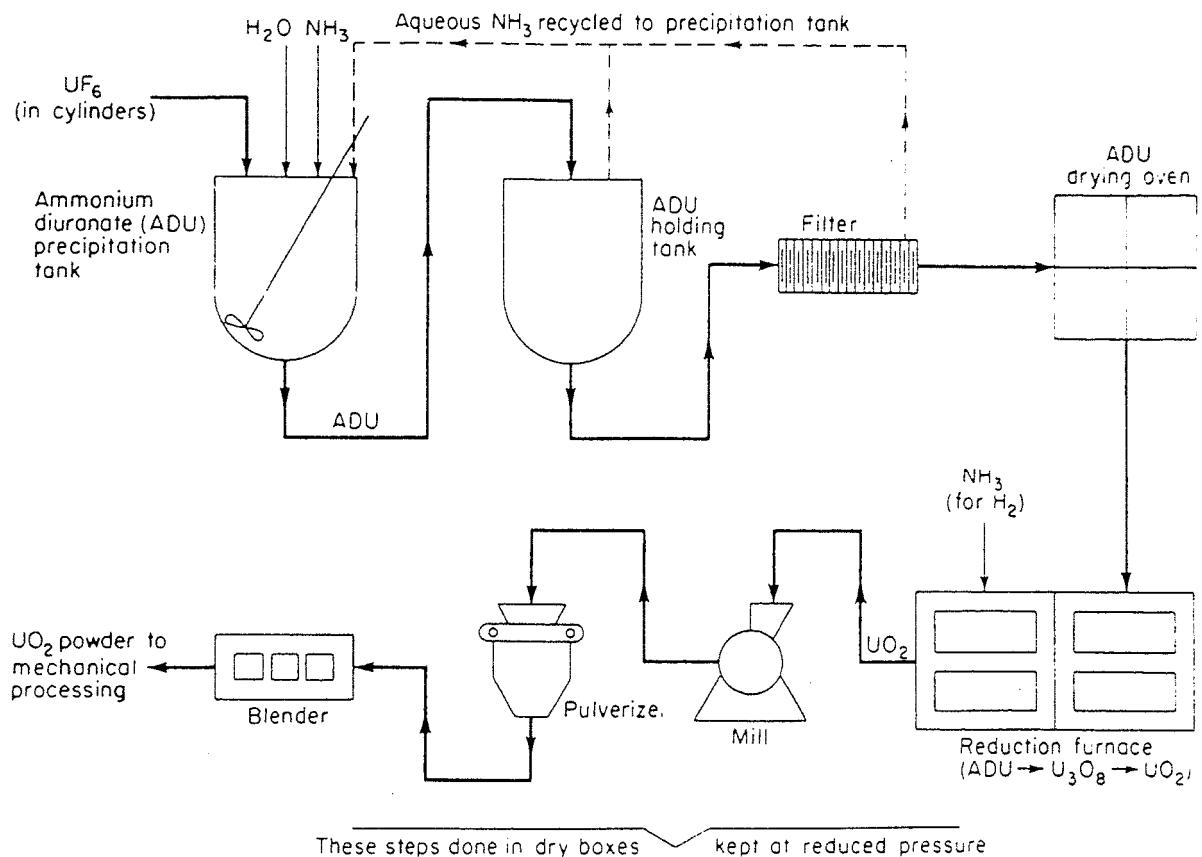


Fig. 21.5. UF_6 to UO_2 by the ammonium diuranate process. (*United Nuclear Corp. and Industrial and Engineering Chemistry.*)

in the United States consumed 4.1 percent of the country's entire electrical power output in 1970. Maximum enrichment is 94% ^{235}U , with a waste containing about 0.3% ^{235}U .

The gas centrifuge process depends on centrifugal force for the separation. Capital expense is greater than for a diffusion plant, but the energy requirement is only $\frac{1}{20}$ th as great. The United States is building a gas centrifuge plant in Portsmouth, Ohio to start operation in 1985 and which will have a capacity of 38 percent of that of the present two gas diffusion plants.

Voigt^{9a} has estimated the 1982 relative costs as \$180 per SWU (separative work units—units of capacity) for the diffusion process with a corresponding cost for the centrifuge process of \$70 to 80 per SWU with the probability of a drop of 20 to 50 percent in the near future.

Other exotic processes continue to be suggested and/or tested. Three such advanced isotope separation (AIS) processes are currently being developed in the United States by the Department of Energy (DOE). These are known as the plasma separation process (PSP), the atomic vapor laser isotope separation (AVLIS) process, and the molecular laser isotope separation (MLIS) process. The cost of a SWU by these processes has been estimated at \$30 to \$40, but much remains to be done and none is likely to be practical before 1990. As nuclear power becomes increasingly important, the expensive separation process will require much expansion, and it is hoped that new processes can reduce costs dramatically.

CONVERSION. UF_6 can be converted to UO_2 through the process shown in Fig. 21.5. A high degree of protection against even minor contamination is essential if the necessary purity is to be obtained.

^{9a} Voigt, op. cit.

Nuclear Fuels Selection

The three fissionable isotopes, ^{233}U , ^{235}U , and ^{239}Pu , have a higher probability of fission than capture when absorbing a neutron. These are the only common materials which can sustain a nuclear fission reaction, and therefore they are the nuclear fuels. Of these isotopes, only ^{235}U occurs in nature. The other two are reactor-synthesized and extend the amount of fissionable material far beyond that which occurs naturally. Fuels for reactor use must have suitable physical as well as nuclear properties. Solids are usually preferred, so UO_2 , ThO_2 , PuO_2 , and mixtures in the form of sintered, high-density pellets are commonly used. Other combinations that have been used are: uranium-aluminum alloys, uranium sulfate solutions, plutonium-aluminum alloys, U_3Si , UC_x , and Pu metal alloys and cermets. UO_2 enriched to varying percentages of ^{235}U is widely preferred because of its high melting point (2176°C), good thermal conductivity, high density, and resistance to the effects of radiation. Fuel is usually prepared from UF_6 enriched to the desired percentage. Figures 21.5 and 21.6 illustrate the steps required.

MECHANICAL FORMING AND ELEMENT FABRICATION. To form fabricated fuel elements, fuels are pressed, sintered; ground to exact size; inserted in a sheath of stainless steel, zirconium, or one of the zircalloys; pressurized with helium; carefully welded shut; then assembled into convenient sized groups for handling. Some work must be done by remote control or in glove boxes. Preparation is tedious and exacting, and quality control is of the utmost importance.

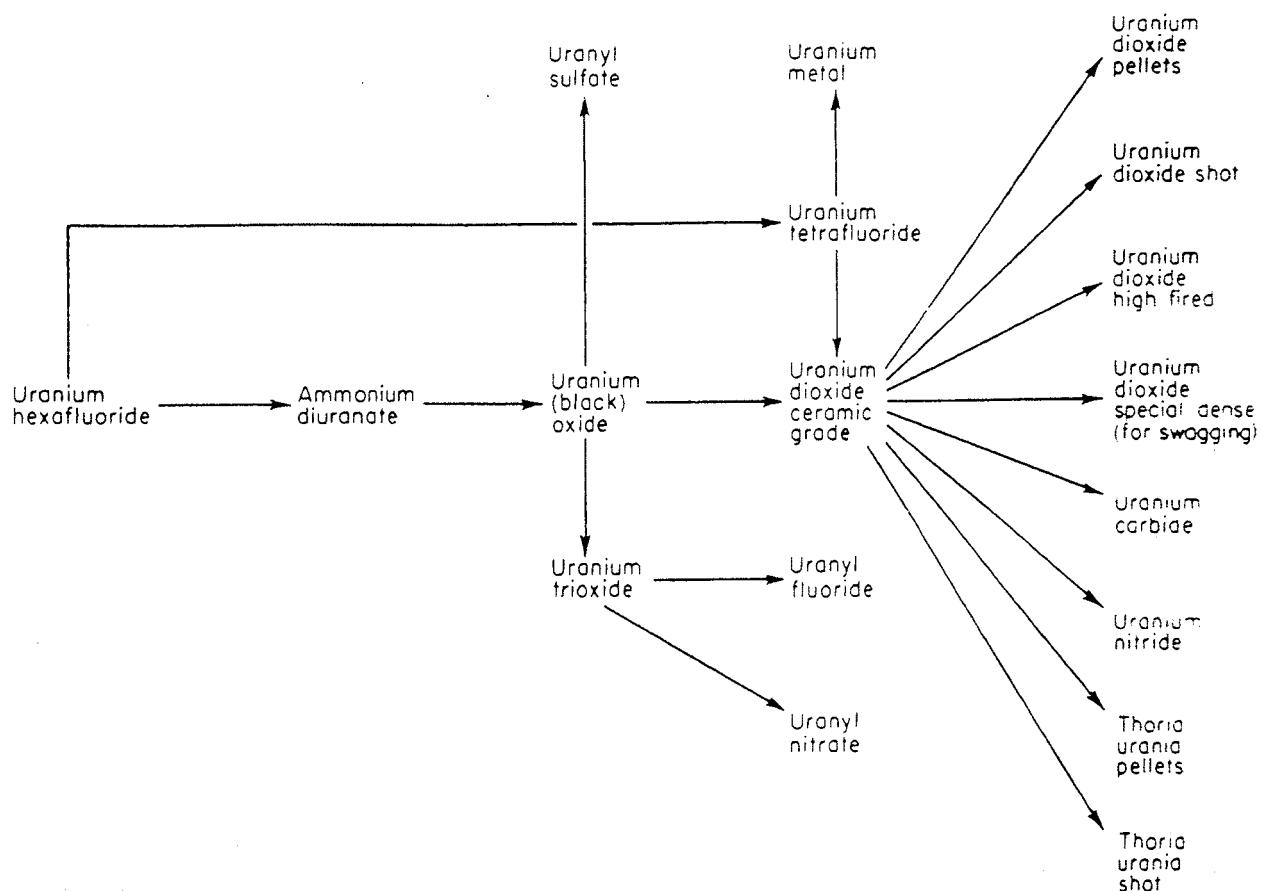


Fig. 21.6. UO_2 production flowchart. (United Nuclear Corp.)

NUCLEAR REACTORS

Nuclear reactors have been defined¹⁰ as devices "containing fissionable material in sufficient quantity and so arranged as to be capable of maintaining a controlled, self-sustaining nuclear fission chain (critical) reaction."

There are three major types of reactors now operating: burners, breeders, and converters. In addition, many other classifications and subgroups are possible.¹¹

BURNERS. Burners commonly use uranium enriched in ^{235}U and some type of moderator to produce heat and slow down the neutrons to maintain the chain reaction. The fuel gradually becomes depleted. See Figs. 21.7 and 21.8.

Figure 21.7 describes the reactor vessel and core. The core consists of approximately 200 nuclear fuel assemblies which are grouped together to make up the core of the reactor. Interspersed among the fuel assemblies are movable control rods, which are made of a material that readily absorbs neutrons. When the control rods are inserted into the core, the nuclear chain reaction in the fuel assemblies is slowed down, and this reduces the amount of heat produced in the core. Withdrawal of the rods speeds up the chain reaction and more heat is produced. The entire reactor core, which contains fuel assemblies and control rods, is enclosed in a heavy stainless-steel vessel. As an added safety feature, the entire reactor assembly is housed in a concrete structure. A liquid coolant is pumped into the reactor vessel to remove heat from the core. The coolant is then pumped out of the reactor vessel and is used to produce steam. Most of the nuclear plants in the United States use ordinary water as a coolant. These plants are known as light water reactors (LWRs).

Fuels currently used consist of natural and enriched uranium, UO_2 , UC_2 , $\text{UO}_2\text{-PuO}_2$, and $\text{UO}_2\text{-ThO}_2$ as rods, plates, pellets, spheres, or pins and clad with zirconium, stainless steel, or other alloys. Heat is carried away from the reactor core by pressurized water, steam, sodium, helium, or CO_2 . Organic liquids and molten salts have been tried but found undesirable. The heat thus removed from the core is then employed to generate steam which runs power-producing turbines, usually coupled to electrical generators. The power train is exactly similar to that used for power generation when the steam produced comes from coal, oil, or gas. Thirty years of experimentation have narrowed the fuel, moderator, heat remover, and liquid combinations but have not shown one set to be completely superior. The types of greatest interest are the pressurized water (PWR), the boiling water (BWR), the gas-cooled (GCR), and the liquid-metal cooled (LMR) reactors. The Canadian CANDU, which is deuterium moderated, and several graphite-moderated units are also in operation.

Figure 21.9 shows one of the many types of reactors being built, a forced circulation BWR which furnishes 420 MW_e. It was designed by the General Electric Co., Atomic Products Division. This reactor was selected as a power producer competitive in all but the lowest cost fossil fuel areas with a conventional boiler system fueled by oil or coal. PWR units in the 1100-MW range are offered by Westinghouse, Babcock and Wilcox, and Combustion Engineering Co. in the United States. France, Canada, Great Britain, and the U.S.S.R. also offer commercial units.

¹⁰ McGraw-Hill Encyclopedia of Science and Technology, vol. 11, McGraw-Hill, New York, 1966.

¹¹ Foster and Wright, *Basic Nuclear Engineering*, 3d ed., Allyn and Bacon, Boston, Mass. 1977.

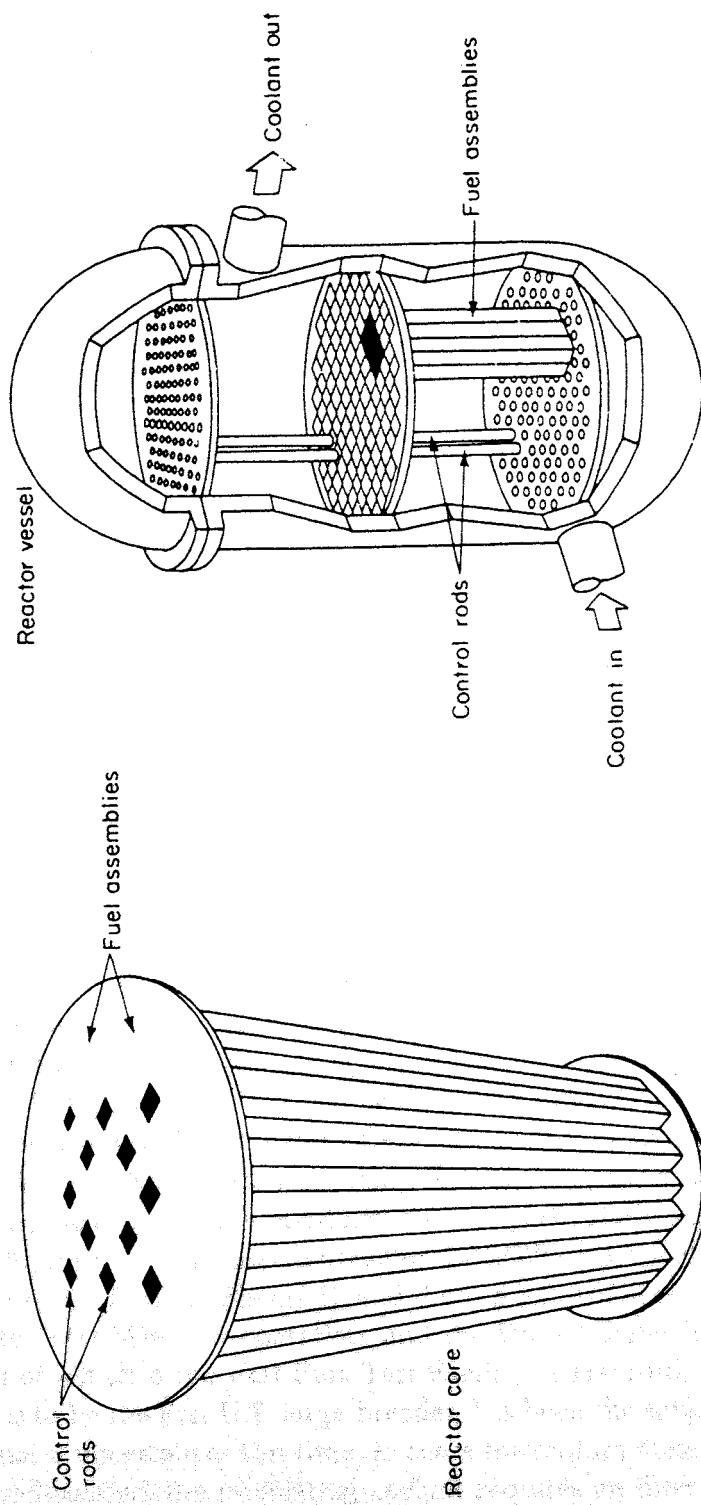


Fig. 21.7. Reactor vessel and core. [U.S. Department of Energy, Publication DOE/NE-0029 (1982).]

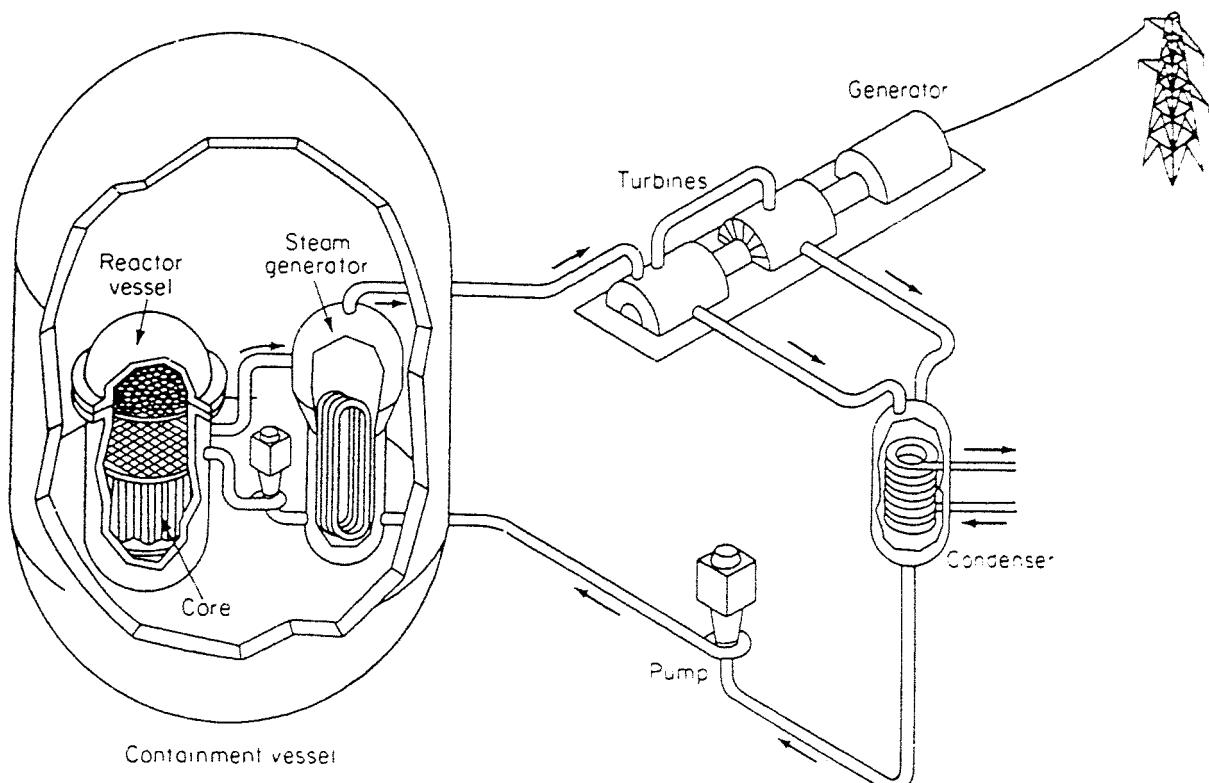


Fig. 21.8. A typical PWR (pressurized water reactor) system. In the pressurized water reactor, the pressure is kept high enough to prevent boiling, even though the water is very hot. The heated water from the core is pumped into a steam generator. Here the heat is transferred to another system and steam is produced. The water from the core is repeatedly circulated through the primary loop, but is never converted into steam. [U.S. Department of Energy, Publication DOE/NE-0029 (1982)]

BREEDERS.¹² Breeders are designed to produce more fuel than they consume. Breeders run without moderators, so the speed of their neutrons is nearly that at which they are expelled after fission. The probability of absorption in the central or core area is small, so the core is surrounded with a blanket of fertile material, usually ^{238}U to absorb the fast neutrons. Fission produces surplus fast neutrons which react with the surround of fertile ^{238}U which then decays to produce plutonium, suitable as a fuel after it has been extracted. Fast reactors are cooled with liquid metals (Na, NaK) because water has relatively poor heat-transfer capability and absorbs too many neutrons. Some combinations are particularly suitable for breeding. The sodium-cooled liquid-metal fast breeder reactor (LMFBR) is particularly favored. The United Kingdom (Dounreay), France (Phenix I), and the U.S.S.R. (BN-600) have several breeders of good size (up to 1600 MW_e) in operation, and the United States has several test units, the most important of which is the Fast Flux Test Facility at Hanford, Wash. The Clinch River reactor, which is to be the first U.S. large breeder, has been the subject of much controversy, and its fate remains uncertain at this time. Because the sodium metal used to cool the reactor core becomes radioactive, the circulating coolant requires an intermediate loop to prevent the escape of radioactivity into the steam loop (see Fig. 21.10). This adds to the cost and complexity of the system, but requires no new technology.

¹²O'Sullivan, Western Europe Pushing Ahead to Develop Fast Breeder Reactors *Chem. Eng. News* 56 (7) 41 (1978); Lepkowski, U.S.S.R. Reaches Takeoff in Nuclear Power, *Chem. Eng. News* 56 (45) 28 (1978).

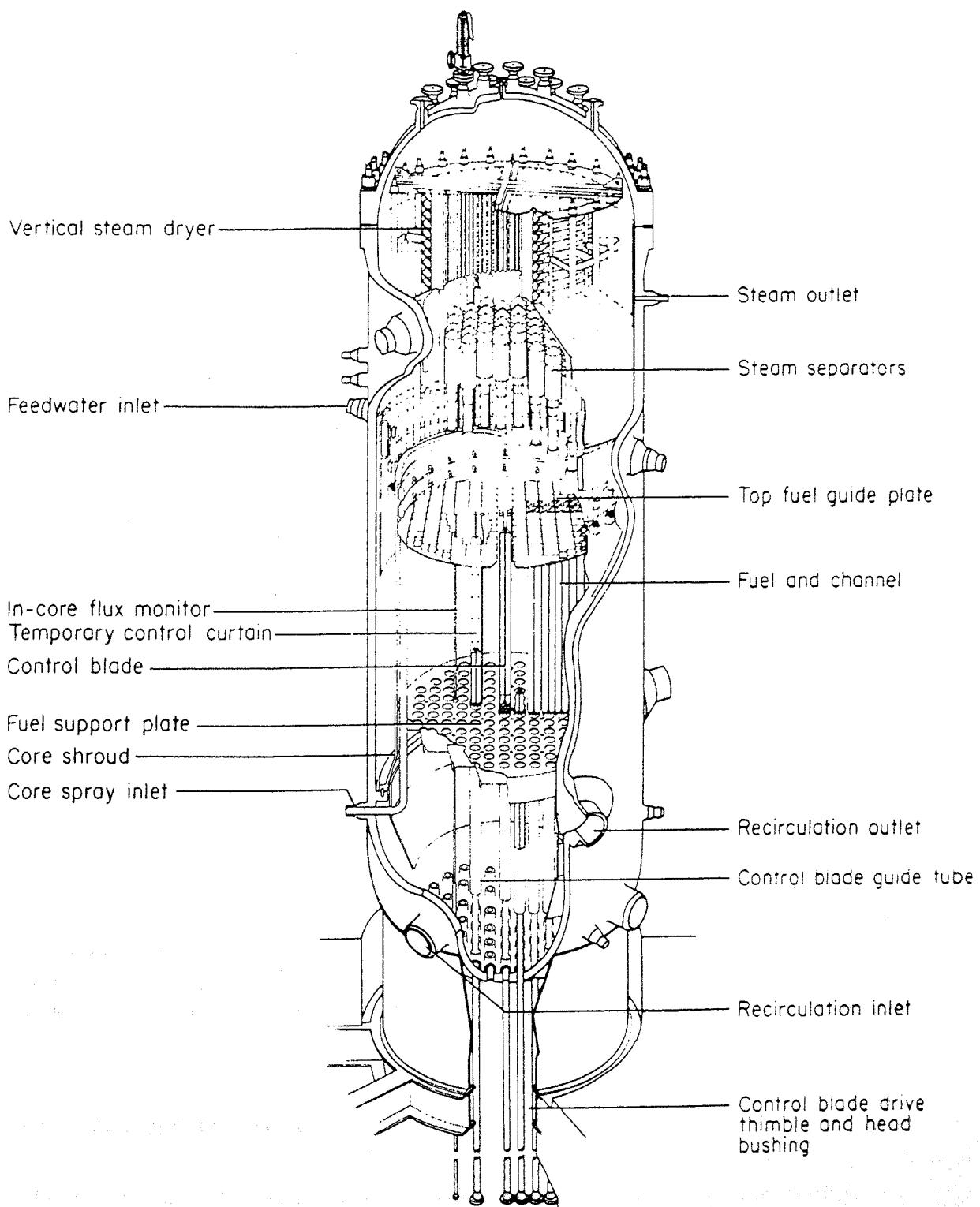


Fig. 21.9. BWR (boiling water reactor) with forced recirculation. Feedwater enters the vessel at the top of the core and, joined by recirculating coolant, flows downward around the core. The recirculation flow, which affords primary control of the load, is fed from the vessel to external pumps, which return it to the bottom of the vessel and up through the core. The generated steam passes through the internal steam separators mounted over the core, through the vertical steam driers, and then from the reactor vessel to the steam turbine. The fuel assemblies are located approximately midway in the reactor vessel. The mechanically driven control rods enter from the bottom of the reactor. The pressure vessel is 5.4 m in diameter and 17.8 m long and has a wall thickness of 18.7 cm.

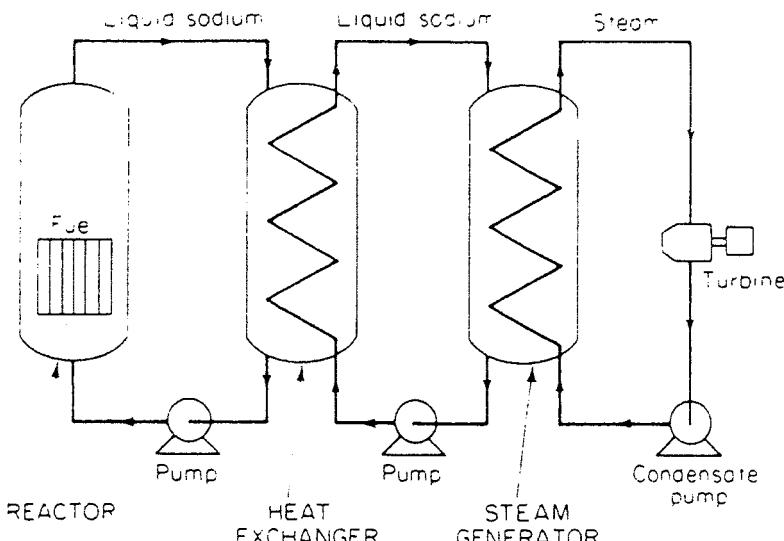


Fig. 21.10. Loop system for fast breeder reactor

The gas (helium)-cooled fast reactor requires no intermediate loop to isolate the coolant from the power stream cycle, but heat interchange is more difficult when gas is used. Operating temperature of this type of reactor is high.

Breeder reactors require chemical processing of a great deal of radioactive material, an expensive process which, among other problems, makes their use for the production of electrical power questionable economically.

CONVERTERS. Converters use ^{238}U as a fertile material to produce ^{239}Pu and are usually not designed to produce useful heat. Cores are smaller and have a longer life than power-producing units. Most military production units are of this type.

ATOM BOMBS. Atom bombs are designed to produce enormous amounts of energy in a very brief time. Fissionable materials are driven into a compact mass by explosive force, irradiated with many neutrons, and held together as long as possible, thus producing large blast effects.

FUSION REACTIONS

The conversion of hydrogen to helium converts matter into energy. For example:



This reaction, which takes place continuously in the sun, is being attempted by physicists. Actual nuclear fusion is more complicated than the simple reaction shown here. The energy produced is very great: $792 \times 10^6 \text{ MJ}$ per kilogram of hydrogen converted. Short bursts of power have been obtained in advanced fusion apparatus, but a reaction sustained enough to permit significant power production has not been achieved. This development appears uncertain and may be many years away.

FUSION¹³

While not yet a commercial part of nuclear technology, fusion of atoms to form more complex ones can be accompanied by loss of mass with the consequent generation of energy. A great deal of expensive experimentation has as yet failed to discover a fusion system in which there is a usable net generation of energy. Scientists feel that real progress is being made, however.

The most promising fuels are deuterium and tritium, sources far less limited than uranium, thorium, oil, or coal. Fusion-fission units have also been suggested. With such units, neutrons from a fusion reactor are used to breed ^{239}Pu from ^{238}U or ^{233}U from thorium. A blanket containing fertile material, kept below critical size, would breed fissile material for use in thermal fission reactors.

PROCESSING NUCLEAR MATERIALS¹⁴

Since the original intent of nuclear reactors was to produce plutonium for military purposes, procedures for separating uranium and plutonium from the radioactive fission products present in spent fuel elements were developed early. These are processes involving solution of fuel elements as nitrates and separation using tributyl phosphate solvent (Purex process), or the obsolete redox process using methyl isobutyl ketone (hexone). There is also a Thorex process for thorium cycle units. Fuel elements from military production units differ markedly in Pu content from spent power units, but a typical spent fuel element from a reactor contains only 0.8% ^{235}U and a roughly similar amount of ^{239}Pu , so a large quantity of material must be handled to produce very little product. The expensive element sheath is destroyed and cannot be reused. A substantial range of isotopes, both stable and radioactive, are present. Many species present are radioactive. Currently recycling is only marginally acceptable politically and perhaps economically, but it is not likely to remain so. To prevent proliferation of nuclear weapons, the United States has taken a stand against fuel reprocessing, which may well prove economically difficult to maintain.

The flowchart of Fig. 21.11 describes the recovery plant of the U.K. Atomic Energy Authority at Windscale which uses the TBK-Kerosene process. After being dissolved in aqueous HNO_3 , the fission products are separated by extracting the uranium and plutonium nitrates in an organic solvent, tributyl phosphate (TBP) and kerosene. This leaves the fission contamination products as "aqueous raffinate to the evaporator plant." The second solvent extraction is mainly for the separation of uranium from plutonium; it is effected by adding ferrous sulfamate to reduce Pu^{4+} to Pu^{3+} , a cation unable to form strong complexes with TBP and consequently removed from the organic uranium stream. The aqueous plutonium solution is oxidized to the Pu^{4+} stage (HNO_3 and NaNO_2), so that plutonium can be extracted

¹³Kulcinski and Burleign (eds.), *The Technology of Controlled Nuclear Fusion*, vol. IV, NTIS, U.S. Dept. of Commerce, 1976; Choi (ed.), *Engineering Problems of Fusion Research*, vols. 1 and 2, IEEE, Piscataway N.J., 1981.

¹⁴Addinall and Ellington, *Nuclear Energy in Perspective*, Kogan Page, London, 1982.

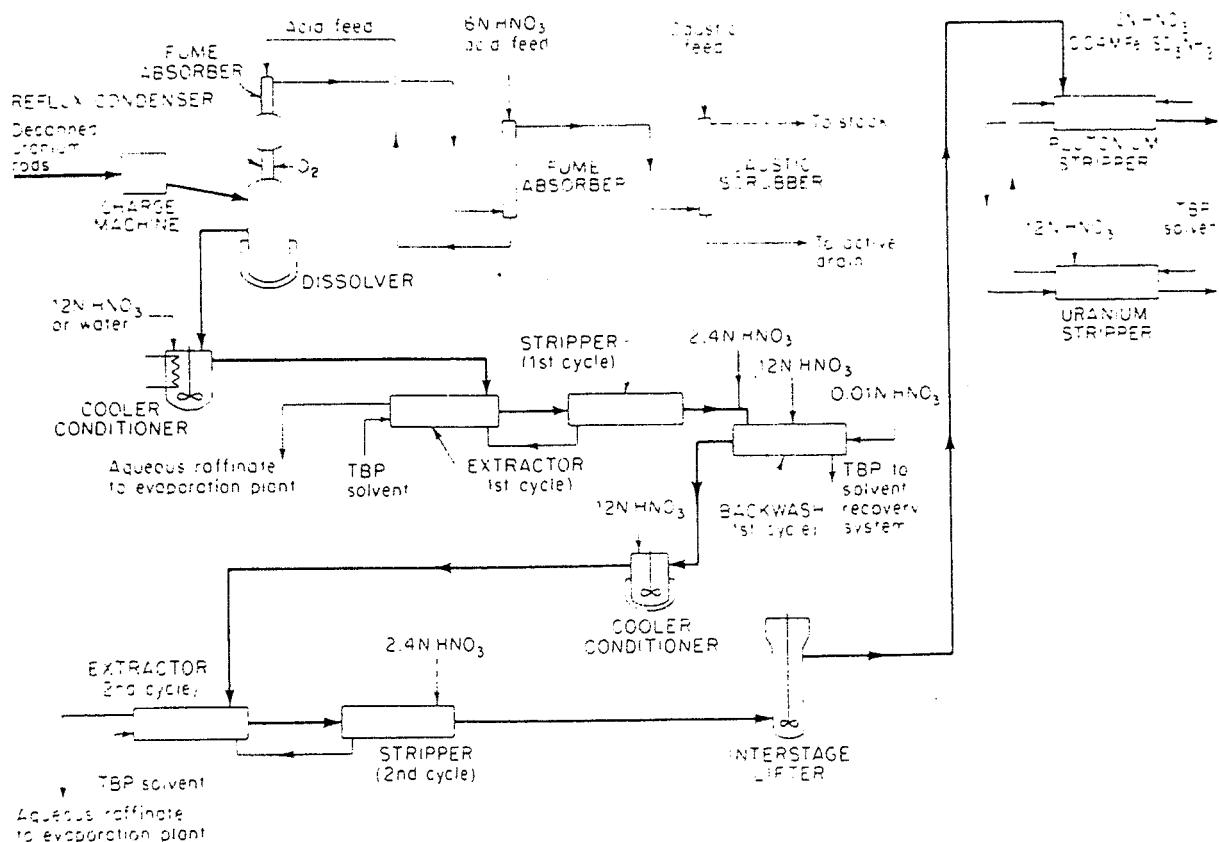
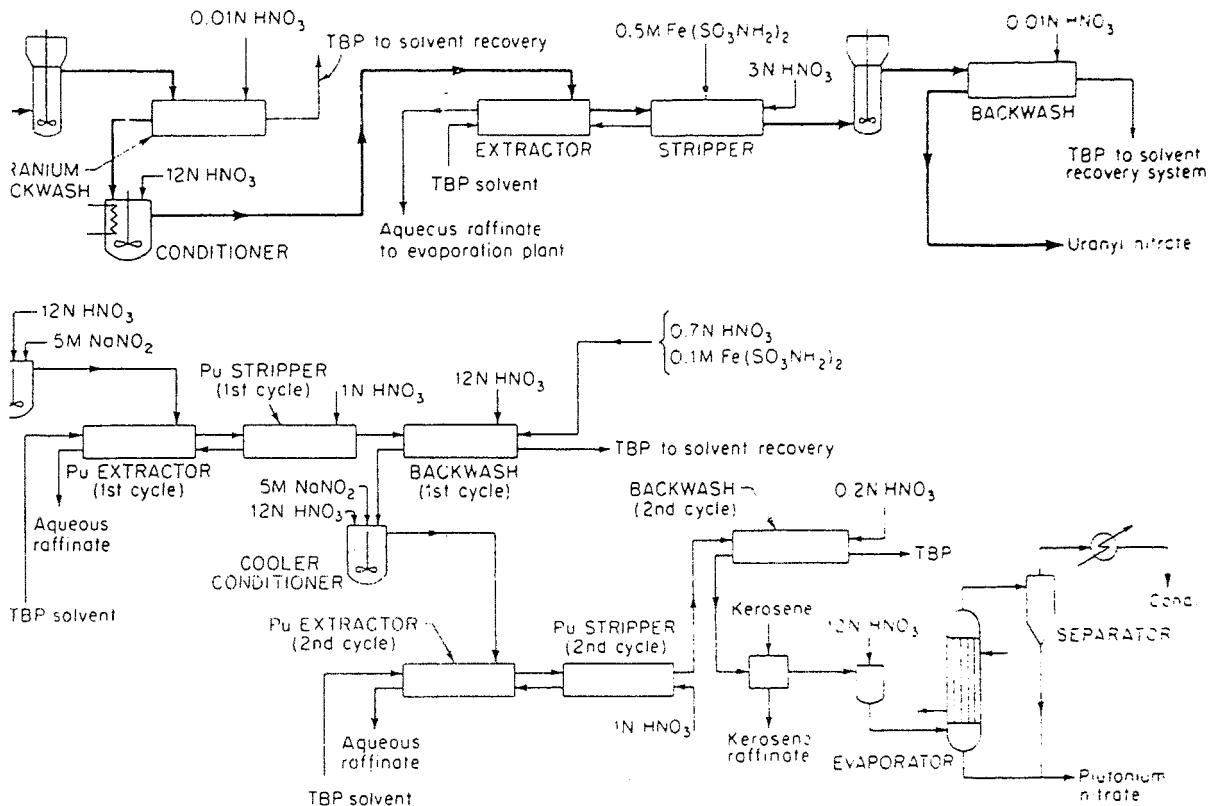


Fig. 21.11. Plutonium and uranium separation via solvent extraction from spent nuclear fuels. [For Details, see Chem. Eng. 71 (25) 148 (1964).]

with TBP from its residual fission products (aqueous raffinate). Successive acidification-oxidation and solvent extraction, followed by a kerosene washing evaporation, furnishes a pure solution of plutonium nitrate. Uranium purification, after separation from the Pu³⁺, transfers the still impure uranium in the TBP stream by an extractive "backwash" into a dilute HNO₃ aqueous solution, and the TBP is recovered. Next another TBP extraction is used to remove uranium after a 3 N HNO₃ acidification, and a second ferrous sulfamate reduction to remove traces of water-soluble impurities (plutonium, etc., as "aqueous raffinate to evaporation plant"). Finally, extraction from the TBP solvent with a 0.01 N HNO₃ solution results in a pure aqueous solution of uranyl nitrate, which is denitrated to UO₃. Such processes require extreme precautions to protect the persons working around them from radiation hazards and use several feet of dense concrete to protect the workers. Work within such units (called cells) is frequently carried out by remote control.

There are currently no commercial reprocessing plants¹⁵ in the United States, although one is built but unlicensed. Several foreign countries, Belgium, France, Federal Republic of Germany, U.K., India, Italy, Japan, and the U.S.S.R. operate such units. There is fear that plutonium from such plants may fall into the hands of terrorist groups or hostile nations, which restricts their construction.

¹⁵O'Donnell, Sandberg, and Brooksbank, Restoring Commercial Reprocessing in the United States, *Nucl. Eng. Int.* **27** (381) 30 (1982).



ISOTOPES¹⁶ AND ISOTOPE SEPARATION

The existence of stable isotopes was known before nuclear technology developed, but the nuclear industry has given great impetus to isotope separation and use. Nuclear reactor transmutation ability has made isotope manufacture almost commonplace. Major isotopes isolated are: ²³⁵U, D₂O for use as an efficient moderator, ¹⁰B for reactor control and safety rods, ⁹⁰Sr and ¹³⁷Cs for food and sewage sterilization, and tritium and ⁸⁵Kr for compact portable light sources. The list is long and growing longer as defense wastes are studied in detail. Defense wastes are the residues from the defense production cycle.

Production of isotopes by planned transmutation is possible, but economical processes for large quantities more frequently involve the separation of naturally occurring elemental mixtures or their extraction as by-products. Defense wastes have come under study as isotope sources for several reasons: (1) The material is present and troublesome to store, (2) the storage problem can be reduced if certain strong heat and/or radiation emitters are isolated and handled separately and, (3) they are a treasure house of materials rare or absent in nature for which important uses may exist. Separation of isotopes is more difficult than ordinary chemical processes, but several techniques are well established. Substantial quantities of isotopes are separated by distillation, chemical exchange, electrolysis, gaseous diffusion, gravitational processes, thermal diffusion, and aerodynamic (nozzle) processes. Other processes known to bring about separation, but now too costly or not yet developed include, photochemical,

¹⁶Villani, Isotope Separation; American Nuclear Society Monograph, American Nuclear Society, Hinsdale, Ill., 1976.

photophysical laser processes, chromatography, adsorption, and electromagnetic and biological processes.

DEUTERIUM. Deuterium has been in great demand and is made on a large scale. As D₂O, its current price is around \$250 per kilogram. Catalytic exchange between hydrogen and water, electrolysis, distillation of liquid hydrogen, exchanges with NH₃, or H₂S, and several other separative processes have been used. Deuterium-producing plants are usually captive to ammonia-producing units because of the availability of large quantities of hydrogen.

¹⁰B. ¹⁰B occurs naturally at 19.8% concentration and is concentrated to 40 to 95% for control rod use by multistage exchange distribution of the weak dimethyl ether complex with the trifluoride. The price is \$4 to \$9 per gram of contained ¹⁰B.

⁷Li. ⁷Li occurs naturally at 92.6% and is concentrated by a method that is currently classified. It sells for about \$3 per gram of contained ⁷Li. Minor quantities of ⁷LiOH are produced because its low affinity for neutrons makes it desirable for the control of the pH of reactor water.

TRITIUM. Tritium, ³H, is made in heavy-water-moderated reactors by the reaction



It is also made by distillation of liquid hydrogen. It is of great interest in nuclear fusion work because its major fusion reaction occurs at a low temperature compared with other substances.

MISCELLANEOUS ISOTOPES. Isotopes may be used as tracers, for studying structural chemistry, in biological, chemical, and physical research, and for geological studies. ⁶⁰Co is used to sterilize hospital medical supplies, foodstuffs, and sewage. ⁹⁰Sr and ¹³⁷Cs are also useful because they emit sterilizing radiation. Tritium and ⁸⁵Kr can be used to provide lights that will function for a long time in remote locations and that require no external source of power. Palladium, rhodium, and ruthenium are also present in substantial quantity in defense wastes and may be economically recoverable.¹⁷ Tracer elements are experimental tools of exceptional diversity and application.

PROTECTION FROM RADIOACTIVITY¹⁸

Radiation hazard is a subject often approached from a highly emotional point of view, probably because radiation cannot be detected by the ordinary human senses. Protection against radiation is possible with insulation (dense concrete, etc.), just as is presently done for hot

¹⁷Jensen, Rohrmann, and Perrig, address before American Nuclear Society, June 1980.

¹⁸Roussin, Abbott, and Bartine (eds.), *Nuclear Reactor Shielding*, Science Press, New York, 1977.